

within the limits of the substance, the surface tension may have time to cause the filament to break from instability.

It would appear, therefore, that any liquid which can be drawn into threads can also produce films, but that the converse is not true, and this seems to agree with observed facts.

Since the explanations which I have put forward in this note depend more on observation than experiment, it is probable that an exact knowledge of the relations of  $n$  and  $k$  might render some modification necessary; but that the separate limits of volume dilatation and shear are the groundwork of the characteristics which are denoted by the adjectives in the list (and many others) is, I think, almost certain.

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*An Investigation of the Spectrum of Ionium.\**

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The preparation of ionium described by Prof. Rutherford in the footnote consisted of a mixture of the oxides of ionium and thorium. The percentage of ionium oxide in the preparation is not known. It can be calculated, however, provided we know both the period of ionium and the number of  $\alpha$ -particles emitted by 1 gm. of the substance per second.

The latter has been determined by Dr. H. Geiger, who found that 1 gm. expelled  $10^8$   $\alpha$ -particles per second. The period, however, is not known with certainty. Soddy has found that, on certain assumptions, it is at least

\* The preparation of ionium examined by Messrs. Russell and Rossi was separated from the actinium residues loaned to me by the Royal Society in 1907. A detailed statement of the methods employed in its separation has been given by Prof. B. B. Boltwood in a paper entitled "Report on the Separation of Ionium and Actinium from certain Residues, and on the Production of Helium by Ionium" ('Roy. Soc. Proc.,' 1911, A, vol. 85, p. 77). The preparation consisted of pure thorium oxide, containing an unknown percentage of ionium oxide. From measurements of the number of  $\alpha$ -particles emitted by the preparation it was concluded that it should contain at least 10 per cent. of ionium, if the period of the latter were not less than 100,000 years. On these data it was anticipated that the preparation should show clearly the strong spectroscopic lines of ionium as well as a complete spectrum of thorium.—E. RUTHERFORD.

100,000 years, and this is the only experimental result that we have at present.

If  $x$  be the percentage by weight of ionium present in the material, and  $y$  the period of ionium in years, then  $x$  and  $y$  are connected by the equation

$$\frac{y}{x} = \frac{3.4 \times 10^{10} \times 1760}{10^8 \times 100},$$

$3.4 \times 10^{10}$  being the number of  $\alpha$ -particles expelled by 1 gm. of radium per second, and 1760 the period of radium in years.

Thus, if the period of ionium be 100,000 years, there is no less than 16 per cent. of ionium oxide in the preparation.

It is well known that ionium and thorium are chemically non-separable. The most persistent efforts, first of Keetman,\* and later of Auer v. Welsbach† and others, have failed to separate these two elements from one another, or to alter the concentration of one of them in the least degree, notwithstanding the sensitiveness of the methods of radioactivity for detecting the slightest change of concentration. For this reason, the conclusion is hardly to be avoided that these two elements are not merely chemically similar, but chemically identical.

It is therefore highly interesting, apart altogether from the interest in obtaining the spectrum of a new body, to examine the influence of a slight difference in the atomic weights of two very similar elements, on so characteristic a property of an element as its spectrum.

Before its spectrum was taken, the ionium preparation was purified from any impurities it might contain by the usual well-known methods of purification of thorium. A quantity of ordinary thorium nitrate was purified also. The most likely impurities in thorium are cerium, lanthanum, and didymium. The only probable impurity in the ionium-thorium preparation is scandium since all others should have been separated completely by the chemical methods employed by Boltwood. The preparation was treated, however, as if every known element were present as impurity.

The strongly ignited oxide was fused in a platinum crucible with potassium bisulphate, the resultant mass powdered, and dissolved in hot water. The ionium and thorium were then precipitated as hydroxide by ammonia, and the precipitate, after being well washed, was dissolved in hydrochloric acid. To this solution was added a strong solution of ammonium oxalate in excess, and the whole diluted to 800 c.c., and, after standing over night, filtered. To the filtrate was added hydrochloric acid in excess, and the ionium-thorium

\* 'Jahr. Radioaktivität,' 1909, vol. 6, p. 269.

† 'Wien Ber.,' 1910, vol. 119 (ii), p. 1011.

oxalate filtered off. The oxalate was converted into hydroxide, and the latter dissolved in hydrochloric acid. The ionium-thorium was precipitated from this solution as hydroxide by means of sodium thiosulphate, this operation being repeated. The solution of the hydroxide, after the second precipitation with thiosulphate, was treated again with ammonium oxalate solution, and the whole series of operations described above was gone through again. After the fourth treatment with sodium thiosulphate, the ionium was precipitated by ammonia and the hydroxide strongly ignited. By this series of chemical processes the ionium-thorium preparation was obtained in a very high state of purity. Two grammes of thorium nitrate were purified by exactly the same methods, and used as comparison body in the spectroscopic work.

Another sample of ionium was purified differently. Ionium was precipitated from a neutral solution by hydrogen peroxide in excess. The precipitate was filtered off, dissolved in nitric acid, and the solution evaporated to dryness. The ionium-thorium nitrate was then dissolved in water, and the precipitation with hydrogen peroxide repeated. The substance was brought into solution again as before, and the ionium-thorium precipitated from a neutral solution by meta-nitrobenzoic acid. The flocculent precipitate was filtered off, dissolved in nitric acid, and the precipitation repeated. The precipitate was then ignited. This second process of purification is simpler than the first, and ensures in the end quite as pure a preparation of ionium-thorium oxide.

The arc spectrum of pure thorium oxide was compared with that of ionium-thorium oxide by photographing the spectra one above the other on the same photographic plate. The region examined extended from  $\lambda = 3800$  to  $\lambda = 5000$ .

The arc was formed between two poles of graphite. A small hole was bored in the lower pole, which was positive, and in it was placed from 40 to 60 mgrm. of the oxide. At first, a small grating of 1 metre radius was used, but later the first order of a Rowland concave grating,  $21\frac{1}{2}$  feet in radius of curvature, was employed. The latter gave a dispersion of 2.6 Ångström units per millimetre on the photographic plate.

With the smaller grating an exposure of 10 seconds was sufficient, and with the larger grating of 4 to 6 minutes.

When the ionium preparation was being burned in the arc, a glass bulb surrounded the poles to prevent loss of the valuable material by spluttering.

Two comparison experiments were carried out with the smaller, and three with the larger grating. In each of the five cases, however, the spectrum of the ionium and thorium was identical with that of pure thorium, except

for the presence of about five of the strongest lines of scandium in the former preparation. Careful examination with a lens revealed no other difference. The scandium lines were much weaker in the ionium preparation purified by the first method than in that purified by the second, showing that some of the scandium had been removed by the chemical processes. The scandium lines were quite marked in the unpurified ionium oxide. Scandium is an element detectable in very small amount, owing partially to its low atomic weight and partially to the great intensity of some of its lines. The amount of it in the preparation was estimated at less than three or four parts in a thousand.

Its presence in the ionium preparation and absence in the pure thorium preparation can be explained easily. Scandium, of all the rare earths, resembles thorium most strongly. Like thorium it is precipitated by hydrofluosilicic acid in acid solution and by sodium thiosulphate. It is readily soluble in alkali carbonates and alkali oxalates. It is also precipitated quantitatively by meta-nitrobenzoic acid, and also to a certain extent by hydrogen peroxide in neutral solution.\* In the pitchblende, from which the ionium was concentrated, some scandium must have been present, and this amount has been concentrated with the thorium and the ionium; in monazite sand, from which the pure thorium is obtained, it is, however, absent.

As ionium was present in the mixture in amount less than could be detected spectroscopically, further experiments were carried out to determine how small a percentage of impurity could be detected with certainty in pure thorium. The bodies chosen for this purpose were  $\text{CeO}_2$  and  $\text{U}_3\text{O}_8$ . The former was selected because it is a rare earth very similar in chemical properties to thorium, and has the same type of spectrum. As bodies of low atomic weight, in general, are detectable spectroscopically in smaller amount than bodies of high atomic weight, the oxide of uranium, whose atomic weight is very similar to that of ionium, was also used as an impurity.

It was found with the larger grating that 1 per cent. of  $\text{CeO}_2$  was very easily detected, and both 2 and 1 per cent. of  $\text{U}_3\text{O}_8$  could be detected with certainty; 0.4 per cent. of  $\text{U}_3\text{O}_8$  could not be detected; 1 per cent. of  $\text{U}_3\text{O}_8$  is just on the limit of detection.

It is natural to expect that the spectrum of ionium is of the same type as the spectra of thorium and cerium, since it is a rare earth, and also that it would be quite distinct and characteristic. Again, a percentage of

\* Sir W. Crookes, 'Roy. Soc. Proc.,' 1908, A, vol. 84, p. 82; R. J. Meyer, 'Zeit. für Anorg. Chem.,' 1908, vol. 60, p. 134.

ionium not greater than that of the  $U_3O_8$  used should be sufficient for its detection in the ionium-thorium preparation.

There is, however, not the slightest trace of any new lines due to ionium. The obvious conclusion, therefore, is that ionium is present in the active preparation to the extent of not more than 1 or 2 per cent.

The maximum value of the period of ionium, therefore, cannot exceed  $\frac{2.0 \times 3.4 \times 10^{10} \times 1760}{10^3 \times 100}$  years, *i.e.* 12,000 years, provided radium is the only transformation product of ionium. There is no experimental evidence which contradicts this maximum value of the period.

Soddy,\* whose work on the growth of radium from purified uranium extending over six years has contributed much to our knowledge of the period of ionium, gives 100,000 years as a minimum estimate, provided that ionium is the only member of the disintegration series between uranium X and radium.

From an entirely different set of experiments on the growth of ionium from highly active preparations of uranium X, the same author concludes that if uranium X is transformed directly into ionium, the period of the latter must exceed 30,000 years.

Our result is consistent with both results of Soddy, if ionium be not the only body between uranium X and radium in the disintegration series. There must be at least one new body preceding ionium. This body has not yet been detected chemically. It does not emit  $\alpha$ -rays, for all the  $\alpha$ -rays emitted by uranium and its products are already accounted for. It is very probably rayless, or it emits soft  $\beta$ -rays only.

Quite recently, Geiger and Nuttall† have shown that there is a relationship between the ranges of the  $\alpha$ -ray products of the uranium-radium series, and the periods of these substances. If the logarithms of the ranges of the  $\alpha$ -rays are plotted against those of the transformation constants, a straight line joining the points is obtained. From this straight line the authors, knowing the range of the  $\alpha$ -ray, have deduced a period of 200,000 years for ionium. This estimate is, of course, independent of any assumption as to whether or not ionium is the only product between uranium X and radium. This value is nearly twenty times greater than the maximum value obtained by us.

The relation of Geiger and Nuttall is, however, merely empirical, and, as they themselves point out, it is not obeyed strictly by radium C. Ionium

\* Summary of Results, given in lecture at Royal Institution on March 15, 1912, 'Nature,' 1912, vol. 89, p. 203; also 'Phil. Mag.,' 1910, vol. 20, pp. 340 and 342.

† 'Phil. Mag.,' 1911, vol. 22, p. 613; 1912, vol. 23, p. 439.

also seems to be an exception. It may, therefore, be said that, while the result of Geiger and Nuttall does not confirm our result, it does not necessarily disprove it.

There are, however, two other possible ways of explaining our failure to obtain a distinct spectrum for ionium, besides the one discussed above.

It is possible that :—

- (1) Ionium has no arc spectrum in the region investigated, or
- (2) Ionium and thorium have identical spectra in the region investigated.

The first possibility is highly improbable, for all solids of high atomic weight have arc spectra, and, further, all rare earths have highly complicated spectra.

The second possibility, though somewhat speculative in nature, is suggested by some recent work on the chemical properties of the radio-elements. There is no evidence at present to disprove its truth. It is well known that there are no less than four sets of long-lived radio-elements, the members of each of which are chemically non-separable. These elements do not all belong to the group of rare earths, many non-radioactive members of which are known to be chemically very similar. Mesothorium, for instance, which is chemically non-separable from radium, belongs to the alkaline earth group. Again, the two non-separable  $\alpha$ -ray products which are present in ordinary uranium, and which have been called by Geiger and Nuttall (*loc. cit.*) uranium 1 and uranium 2, belong to the chromium-molybdenum-tungsten group of elements. The explanation of these striking chemical similarities is very probably that the two very similar bodies are really different members of the same group of elements, the difference in their chemical properties being less pronounced than the differences between other members of the same group, owing to the small difference in their atomic weights. But the possibility that they are identical in all physical and chemical properties, and differ only in atomic weight and in radioactive properties, should not be lost sight of. If this explanation should eventually prove to be justified, the spectrum of ionium would be identical with that of thorium.

#### *Summary.*

The arc spectrum of a highly active preparation of ionium containing thorium has been investigated. No new lines due to ionium have been obtained. From this result it has been deduced that the period of ionium cannot exceed 12,000 years. This result, taken in conjunction with Soddy's results on the period of ionium, points to the existence of at least one new comparatively long-lived body between uranium and ionium in the disintegration series.

We have to thank Prof. Rutherford very much, not only for his constant help and advice, but also for putting facilities for chemical work at our disposal, and for the loan of the very valuable preparation of ionium used in the experiments.

[*Note added November 5, 1912.*—After this research had been completed, and the results communicated to the Royal Society, our attention was drawn to a paper read by Prof. F. Exner and Dr. E. Haschek before the Vienna Academy on June 20, and published in the ‘Wiener Berichte,’ 1912, vol. 121 (iia), pp. 1075–77.

These authors have investigated the spectrum of an ionium preparation separated by v. Welsbach from pitchblende; 1 grm. of this preparation contains approximately two-thirds of the amount of ionium in our preparation. The spectrum was investigated both in the visible and the ultra-violet region of the spectrum. The spectrum obtained showed lines of cerium, scandium, and yttrium, and also of five less common rare earths. No lines, however, could be assigned to ionium. They point out, as we have done, that the period of ionium has been very much over-estimated, and estimate that it may be even less than that of radium. They do not discuss, however, how this result may be reconciled with the estimates of Soddy.]

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